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Title of Invention: Hydrogenated vinyl aromatic hydrocarbon polymer composition and optical disk substrate

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Specifications

1. Title of Invention:

Hydrogenated vinyl aromatic hydrocarbon polymer composition and optical disk
substrate

2. Claims:

(1) A hydrogenated vinyl aromatic hydrocarbon polymer composition with excellent
adhesiveness, characterized in that it is a polymer composition of which

- (a) 0-90 wt % is a polymer which is selected from polymers obtained by hydrogenating 80 mol % of the aromatic rings of vinyl aromatic hydrocarbon polymers, or polymers obtained by graft-reacting said polymers with unsaturated monomers containing polar groups so that the content of the latter is 0.01-10 wt %, and
- (b) 10-100 wt % is a polymer which is selected from polymers obtained by hydrogenating all of the double bonds and 80 mol % or more of the aromatic rings in a vinyl aromatic hydrocarbon-conjugate diene block copolymer, or polymers obtained by graft-reacting said polymers with unsaturated monomers containing polar groups so that the content of the latter is 0.01-10 wt %;

and at least one of the polymers (a) and (b) is a polymer obtained by graft-reacting so that an unsaturated monomer containing a polar group is contained in it with a content of 0.01-10 wt %.

(2) An optical material, composed of the hydrogenated vinyl aromatic hydrocarbon polymer composition of Claim (1).

(3) An optical disk substrate, characterized in that it consists of the hydrogenated vinyl aromatic hydrocarbon polymer composition mentioned in Claim (1).

3. Detailed Explanation of Invention:

Field of Use in Industry

This invention concerns a hydrogenated vinyl aromatic hydrocarbon polymer composition with excellent transparency, heat resistance, and adhesiveness with metals, etc.; in addition, it concerns an optical disk substrate which is obtained by using a hydrogenated vinyl aromatic hydrocarbon polymer composition of this kind.

Conventional Technology

Optical recording using lasers has been intensively developed in recent years, since it makes possible high-density information recording, storage, and play-back. An example of this kind of optical recording is the optical disk. In general, optical disks are fundamentally

composed of transparent substrates and various kinds of recording media coated on them. There are many cases in which colorless, transparent synthetic resins are used as the transparent substrates of optical disks; typical examples of these are polycarbonates (abbreviated below as "PCs") and poly(methyl methacrylate) (abbreviated below as "PMMA"). These resins have excellent colorless transparency and also have excellent properties intrinsic to each of them, but they do not have all of the essential properties required for optical materials, especially optical disk substrates, and therefore have problems which require solution. For example, PCs have the problem of birefringence, caused by their aromatic rings, and they also have the problem of water absorbability or permeability. PMMA, on the other hand, has been found to have various problems, such as its heat resistance, water absorbability, and toughness.

Thus, these resins have been used, despite the problems intrinsic to each of them, but in reality, new problems, which are described below, arise in relationship to the recording media coated on the transparent substrates made with these resins.

On the other hand, with respect to recording media, developments in many directions have been performed related to the applications of the optical disks. For example, among recording and play-back media, referred to as the "write-once" type, there is the type in which holes are made, and among recording/play-back/erase/re-recording media, referred to as the "erasable" type, there is the phase transfer type, which uses the crystal transfer phenomenon, the optomagnetic type, which uses the optomagnetic effect, etc. These recording media materials consist primarily of tellurium and its oxides, synthetic compounds, etc. in the case of the write-once type, and amorphous alloy compounds, etc., of rare earth and transition metals, such as GdFe, TbFe, GdFeCo, and TbFeCo, as well as inorganic materials in the case of the erasable type. In general, they are formed by forming films on the transparent substrates by dry methods, such as sputtering in high vacuums.

The moisture absorbability and water permeability of PCs and PMMA cause problems of warping due to expansion of the substrate itself when it absorbs moisture; on the other hand, however, by allowing moisture to permeate through the substance, decomposition of the recording medium is caused, and this results in a shortening of the life of the optical disk substrate.

Moreover, the heat resistance of the substrate resin causes the following problems. In optical disks, especially those of the write-once and erasable types, the temperature of the optical disk reaches 200°C or higher during writing and erasing. Therefore, even if this heat does not directly fall on the disk substrate, it can be predicted that the substrate will become rather hot during writing and erasing, and resins with low heat resistances can give problems, such as deformation of the substrate or deformation of groups.

On the other hand, in the process of manufacturing optical disks, heat treatment processes are frequently included in order to prevent the substrates or recording media from changing over time, but in order to improve productivity, it is desirable to shorten the processing time by performing the treatment at as high a temperature as possible. From this point of view, if the heat resistance of the resin is low, a high treatment temperature cannot be employed, and the productivity cannot be increased.

Therefore, PMMA, which has a low heat resistance, is completely inadequate for withstanding the high temperatures of the optical disk production process or the conditions under which optical disks are used, and PCs, which have higher heat resistances, have been the main materials investigated up to now as transparent substrate materials. However, even PCs have been evaluated as not necessarily having sufficient heat resistances, and the appearance of resin materials with higher heat resistances is desired.

As a way of compensating for the drawbacks in conventional resins, such as PCs and PMMA, there is the method of using transparent resins composed primarily of carbon and hydrogen and having high softening points; the inventors of this invention have already proposed hydrogenated vinyl aromatic hydrocarbon polymers in Japan Patent Application No. 63-149845, etc.

Problems Which This Invention Seeks to Solve

However, the aforementioned hydrogenated vinyl aromatic hydrocarbon polymers are included in the category of the so-called "polyolefins," which have low adhesivenesses, and there has been the problem that they have poor adhesiveness with recording films and cannot provide sufficient lifetimes for optical disks.

Means for Solving These Problems

Therefore, the inventors performed careful investigations concerning improved resins for increasing the adhesiveness with the aforementioned recording film layer. As a result, they discovered that, by using a polymer composition obtained by graft-polymerizing an unsaturated monomer containing a polar group to one or both of a hydrogenated vinyl aromatic hydrocarbon polymer and a hydrogenated vinyl aromatic hydrocarbon-conjugate diene block copolymer, it is possible to obtain an optical disk substrate which retains the high heat resistance of the original hydrogenated vinyl aromatic hydrocarbon polymer and also has excellent adhesiveness with the recording film layer. Thus, this invention was achieved.

That is, the gist of this invention is that it is a hydrogenated vinyl aromatic hydrocarbon polymer composition with excellent adhesiveness, characterized in that it is a polymer composition of which

- (a) 0-90 wt % is a polymer which is selected from polymers obtained by hydrogenating 80 mol % of the aromatic rings of vinyl aromatic hydrocarbon polymers, or polymers obtained by graft-reacting said polymers with unsaturated monomers containing polar groups so that the content of the latter is 0.01-10 wt %, and
- (b) 10-100 wt % is a polymer which is selected from polymers obtained by hydrogenating all of the double bonds and 80 mol % or more of the aromatic rings in a vinyl aromatic hydrocarbon-conjugate diene block copolymer, or polymers obtained by graft-reacting said polymers with unsaturated monomers containing polar groups so that the content of the latter is 0.01-10 wt %;

and at least one of the polymers (a) and (b) is a polymer obtained by graft-reacting so that an unsaturated monomer containing a polar group is contained in it with a content of 0.01-10 wt %.

The resin composition of this invention is especially suitable as an optical disk substrate.

This invention will be explained in detail below.

The first ingredient of the composition of this invention is a hydrogenated vinyl aromatic hydrocarbon polymer.

As the vinyl aromatic hydrocarbon which is used as the monomer, one can use styrene, p-methylstyrene, α -methylstyrene, etc.; styrene is a particularly typical example of these compounds.

As the vinyl aromatic hydrocarbon polymer, one can use a homopolymer consisting of 1 of these vinyl aromatic hydrocarbons, or a copolymer of 2 or more of them. The polymerization method used is not particularly limited, as long as an amorphous polymer can be obtained, but ordinarily, radical polymerization, anionic polymerization, etc., are used. Moreover, one can use a copolymer obtained by copolymerizing it with other monomers which are copolymerizable with it, in a range in which the properties of the vinyl aromatic hydrocarbon polymer are not lost. Examples of such monomers are acrylic acid, acrylic acid esters, methacrylic acid, methacrylic acid esters, maleic acid, maleic anhydride, acrolein, vinyl esters, vinyl ethers, vinyl ketones, acrylonitrile, etc.

The molecular weight of this raw material vinyl aromatic hydrocarbon polymer should be 50,000 or more, as a number average molecular weight. If the molecular weight is too low, the heat resistance and toughness of the resin obtained after the hydrogenation will be reduced. There is no particular upper limit to the molecular weight, but ordinarily it is 400,000 or less.

The hydrogenated vinyl aromatic hydrocarbon polymer used in this invention can be obtained by ring-hydrogenating a vinyl aromatic hydrocarbon polymer of this type in the presence of a hydrogenation catalyst which has the function of hydrolyzing aromatics. Examples of the hydrogenation catalysts used in this case are metals such as nickel, cobalt, ruthenium, rhodium, platinum, palladium, etc., or their oxides, salts, complexes, and catalysts made by supporting them on supports such as active carbon, diatomaceous earth, alumina, etc. Among these, carbon- or alumina-supported Raney nickel, Raney cobalt, stabilized nickel and ruthenium, rhodium, or platinum catalysts are desirable from the point of view of reactivity.

The ring hydrogenation reaction should be performed under a pressure of 50-250 kg/cm² and at a temperature of 100-200°C, using as the solvent a saturated hydrocarbon solvent, such as cyclohexane, methyl cyclohexane, n-octane, decalin, tetralin, naphtha, etc., or an ether solvent such as THF.

The hydrogenation rate of the aromatic rings in the ring hydrogenation reaction should be 80 mol % or higher. If the hydrogenation rate is low, the heat resistance will be reduced, and the birefringence, as an optical material, will become high, which is not desirable. The ring hydrogenation rate of this ingredient is ordinarily 90 mol % or higher, preferably 95 mol % or higher.

The molecular weight of the hydrogenated vinyl aromatic hydrocarbon polymer obtained in the manner described above is 50,000-300,000, preferably 50,000-150,000, as a number average molecular weight.

The vinyl aromatic hydrocarbon polymer segment in the vinyl aromatic hydrocarbon-conjugate diene block copolymer which is the raw material of the vinyl aromatic hydrocarbon-conjugate diene block copolymer used in this invention may be the same as the aforementioned vinyl aromatic hydrocarbon polymers. Moreover, as the conjugate diene in the conjugate diene polymer segment, one can use 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, etc. In particular, 1,3-butadiene and isoprene are generally used. Block copolymers consisting of 2 or more of these segments can be obtained easily by the publicly-known method called "living anionic polymerization"; for example, one can use a method of polymerizing in a hydrocarbon solvent such as hexane or heptane, with an organic lithium compound as the initiator. The content of the vinyl aromatic hydrocarbon polymer segment in this block copolymer should be 20 wt % or higher, preferably 40 wt % or higher, and especially preferably 60 wt % or higher. Moreover, the content of the conjugate diene polymer segment should be 20 wt % or less, preferably 10 wt % or less, of the total composition of this invention.

If the content of the conjugate diene polymer segment in the composition is too great, the heat resistance and toughness of the composition will be reduced, and it will be unsuitable as an optical disk substrate.

The molecular weight of the raw material vinyl aromatic hydrocarbon-conjugate diene block copolymer of this kind is 30,000-400,000, preferably 50,000-400,000, as a number average molecular weight.

The hydrogenation of the vinyl aromatic hydrocarbon-conjugate diene block copolymer may be performed by the same methods as the aforementioned hydrogenation, since the hydrogenation of the conjugate diene polymer segment is ordinarily easier than the hydrogenation of the aromatic rings. With respect to the hydrogenation rate, the hydrogenation rate of the double bonds from the conjugate diene segment is essentially 100%. With respect to the hydrogenation rate of the aromatic rings, the lower limit of the hydrogenation rate of the aromatic rings is 80 mol % or more, preferably 90 mol % or more, and especially preferably 95 mol % or more. If the ring hydrogenation rate is lower than the aforementioned values, the heat resistance will be reduced, the birefringence will be increased, and the miscibility with the first ingredient will be reduced.

The molecular weight of the hydrogenated vinyl aromatic hydrocarbon-conjugate diene block copolymer obtained in the manner described above is 20,000-300,000, preferably 50,000-150,000.

The unsaturated polar monomers which are graft-reacted with the hydrogenated vinyl aromatic hydrocarbon polymer or the hydrogenated vinyl aromatic hydrocarbon-conjugate diene block copolymer of this invention may be monomers which undergo radical reactions; in particular, α,β -unsaturated carboxylic acids or their derivatives are preferable. For example, one can use acid anhydrides such as maleic anhydride, nadic anhydride, etc.; maleimides, such as N-phenylmaleimide, N-cyclohexylmaleimide, etc.; esters, such as methyl acrylate, methyl methacrylate, etc.; or epoxies, such as glycidyl acrylate, glycidyl methacrylate, acrylglycidyl ether, etc. These polar monomers can be used in the modified polymer in the range of 0.01-10 wt %, preferably 0.05-5 wt %, and especially preferably 0.05-5 wt %, with respect to the polymer. If the graft polymerization quantity is too small, there will be no adhesiveness with the sputtered film, and if the graft polymerization quantity is too great, the low moisture absorbability will be harmed.

Examples of the radical initiator used in the radical reaction of this invention are organic peroxides, such as α,α' -bis(*t*-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(*t*-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexyne-3, benzoyl peroxide, di-*t*-butyl peroxide, etc. or azo compounds, such as α,α' -azobis(isobutyronitrile), etc. These radical initiators are used in the proportion of 0.001-20 wt %, preferably 0.1-5 wt %, with respect to the polymer.

Examples of the solvents used in this invention are halogenated aromatic hydrocarbons, such as chlorobenzene, o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene, etc.; aromatic hydrocarbons, such as benzene, toluene, xylene, naphthalene, tetralin, isopropylbenzene, *t*-butylbenzene, etc.; aliphatic hydrocarbons, such as cyclohexane, methyl cyclohexane, decalin, etc.; or ethers, such as tetrahydrofuran, etc. One may use any solvents which are ordinarily used in radical reactions and which dissolved grafted polymers, but benzene, toluene, etc., are especially desirable from the points of view of removing the catalyst and the efficiency of the graft reaction. These solvents are used in the proportion of 2-200 liters, especially 3-30 liters, per kilogram of the grafted polymer.

The reaction temperature and reaction time in the graft reaction of this invention are determined by considering the half-life of the radical initiator used, etc., but it is preferable to use a temperature and time such that the decomposition rate of the radical initiator is 50% or higher. Ordinarily, the reaction temperature is in the range of 50-200°C, preferably 70-150°C. If the temperature is lower than this lower limit, the graft reaction will be insufficient, and if it is higher than the upper limit, problems such as discoloration, gelling, or a marked reduction in the molecular weight will arise. Moreover, the reaction time is generally 0.5-5 hours, but it is not limited to this range.

The graft reaction is performed in such a way that the reduction in molecular weight or gelling due to the graft reaction is kept as low as possible.

0-90 wt %, preferably 0-80 wt %, of the hydrolyzed vinyl aromatic hydrocarbon polymer or its graft product and 10-100 wt %, preferably 20-100 wt %, of the hydrolyzed vinyl aromatic hydrocarbon-conjugate diene block copolymer or its graft product are blended. The blending method may be the molten blending method, the solution blending

method, etc., as long as this composition is thoroughly mixed.

The resins obtained as described above are ordinarily compounded with a thermal stabilizer and molded.

As the thermal stabilizer, one can use a hindered phenol-type thermal stabilizer, a sulfur-type thermal stabilizer, a phosphorus-type thermal stabilizer, etc.

It is desirable to use a combination of a hindered phenol-type thermal stabilizer and a phosphorus-type thermal stabilizer, from the point of view of increasing the resistance to thermal deterioration.

Examples of hindered phenol-type thermal stabilizers which can be used in this invention include tetrakis[methylene-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate methane, 3,9-bis[1,1-dimethyl-2- β -(3-*t*-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane, 1,3,5-tris(3,5-di-*t*-butyl-4-hydroxybenzyl-s-triazine-2,4,6(1H, 3H, 5H)-trione, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, etc.

Examples of the phosphorus-type thermal stabilizers include tetrakis(2,4-di-*t*-butylphenyl)-4,4'-biphenylene phosphonite, bis(2,6-di-*t*-butyl-4-methylphenyl)pentaerythritol diphosphite, etc.

Suitable quantities in which these stabilizers may be added are 0.01-1 part by weight each.

The method of mixing these stabilizers and the resin composition of this invention is not especially limited, but ordinarily it may be done by mixing the resin and the stabilizer with a ribbon blender, tumbler blender, Henschel mixer, etc., and then melting and kneading them with a Banbury mixer, single-screw extruder, double-screw extruder, etc., forming pellets. To obtain optical disk substrates, for example, injection molding is performed, using the pellets obtained in this manner, at a molding temperature of 270-350°C, preferably 280-340°C. In this manner, optical disk substrates can be obtained with excellent transparency, heat resistance, etc., no discoloration, and extremely small optical distortion.

In making optical disks by using the optical disk substrates obtained from the hydrogenated vinyl aromatic hydrocarbon polymer composition of this invention, a film of SN_x , TaO_x , etc., may be formed on the surface of the substrate by sputtering or vacuum deposition, etc., and a recording layer made of TbFeCo , etc., is formed on top of this; finally, this layer is covered with a protective layer.

Effectiveness of Invention

The optical disk substrates obtained by using the composition of this invention have excellent adhesiveness with the recording layer; therefore, one can obtain sufficient lifetimes for optical disks.

Moreover, since the polymer composition of this invention has excellent heat resistance and optical properties, it can also be used for other molded materials besides optical disks. In such cases, also, the excellent adhesiveness of the polymer composition of this invention is effective.

Actual Examples

This invention will be explained in further detail below by giving actual and comparison examples, but it is not limited by the actual examples below as long as its gist is preserved.

Furthermore, the various properties in the actual examples and comparison examples below were measured by the following methods:

(1) Number average molecular weight:

Measured in the same manner as polystyrene, by gel permeation chromatography (GPC); the number average molecular weight converted to polystyrene was obtained.

(2) Ring hydrogenation rate (%):

The poly(vinyl cyclohexane) resin was dissolved in tetrahydrofuran (THF) and measured by UV absorption.

(3) Softening point (°C):

Using a thermomechanical analyzer made by Dupont Co., the softening point was measured with a load of 5 g and a 5°C/min temperature rise rate, using a needle insertion mode probe. The thickness of the test pieces was 3 mm.

Resin Manufacturing Example 1

A styrene homopolymer (Mitsubishi Monsanto Chemical Industries Co., HH-102, number average molecular weight 100,000) was dissolved in tetrahydrofuran and 5% Pd/C was added as a catalyst; a hydrogenation reaction was performed for 6 hours at a temperature of 170°C and under a hydrogen pressure of 100 kg/cm². A hydrogenated polystyrene with a number average molecular weight of 68,000 and a ring hydrogenation rate of 99.0% was obtained.

Resin Manufacturing Example 2

Hydrogenation was performed in the same manner as in Resin Manufacturing Example 1, except that a styrene-butadiene block copolymer (number average molecular weight 100,000, butadiene content 20 wt %) obtained by anionic polymerization was used. A hydrogenated styrene-butadiene block copolymer with a number average molecular weight of 87,000 and a ring hydrogenation rate of 99.6% was obtained.

Resin Manufacturing Example 3

Hydrogenation was performed in the same manner as in Resin Manufacturing Example 1, except that a styrene-butadiene block copolymer obtained by the anion polymerization method (number average molecular weight 105,000, butadiene content 5 wt %) was used. A hydrogenated styrene-butadiene block copolymer with a number average molecular weight of 89,000 and a ring hydrogenation rate of 93.5% was obtained.

Actual Example 1

Three kg of the hydrogenated styrene-butadiene block copolymer obtained in Resin Manufacturing Example 2 and 21 liters chlorobenzene were charged into a reactor, and the temperature was raised to 125°C while stirring, under nitrogen. A solution of 600 g maleic anhydride and 18 g dicumyl peroxide dissolved in 9 liters chlorobenzene was added to the aforementioned reactor; the whole solution was added in 1 hour and a half. The stirring was continued at 125°C for 3 hours longer to perform the reaction sufficiently.

After cooling, the maleic-anhydride-modified polymer obtained was precipitated in acetone and washed repeatedly with acetone, and the unreacted maleic anhydride, the organic peroxide, and its decomposition products were removed. A maleic-anhydride-modified hydrogenated styrene-butadiene block copolymer was obtained, in the form of a white powder. When the infrared absorption spectrum of this polymer was measured, an extremely evident absorption appeared at 1784 cm^{-1} , the characteristic peak of the acid anhydride; thus, it was clearly observed that maleic anhydride was bonded to the polymer. The maleic anhydride content was 1.57 wt %. Moreover, the number average molecular weight before the graft reaction was 88,000, but it was 81,000 after the reaction; the decrease in molecular weight due to the reaction was extremely small.

Two kg of the maleic-anhydride-modified hydrogenated styrene-butadiene block copolymer obtained in this manner and 3 kg of the hydrogenated polystyrene obtained in Resin Manufacturing Example 1 were dissolved in tetrahydrofuran and then precipitated in methanol. To the wet powder obtained in this manner, 0.2 part by weight 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene (Nippon Chiba Geigy Co., Irganox 1330) and 0.2 part by weight (2,6-di-*t*-butyl-4-methylphenyl)pentaerythritol diphosphite (Adeca Argus Co., Markpep-36) were added, after which the result was dried. Next, pellets were made with an extruder. These pellets were molded to produce circular-plate-shaped disk substrates 1.2 mm thick and 130 mm in diameter by using an injection molder (Naki Co. M140A), with a grouped stamper attached to the movable mold side, at a resin temperature of 300°C.

The softening point of the substrate resin was 168°C, and its bending modulus was 25,000 kg/cm². The substrate obtained was put into a sputtering device and the atmosphere was evacuated to 8×10^{-7} torr or less, after which reactive sputtering was performed with a Ta target, using a mixed Ar/O₂ gas. An interference layer composed of Ta₂O₅ (800 angstroms thick) was formed. Next, double simultaneous sputtering was performed with Ar gas, using a Tb target and an FeCo target, forming a TbFeCo recording layer (300 angstroms thick). Furthermore, a reflective layer 300 angstroms thick was formed by sputtering in Ar gas with an Al target, on which a Ti chip was placed. A mirror surface was made on part of the substrate on which this film was formed; 10 lines in each direction were drawn on it in a 1 cm x 1 cm part, in a checker-board pattern, and adhesive tape made by the Teraoka Co. (imido film base) was stuck to this part. By pulling it off, the adhesive force between the substrate and the tantalum oxide film was evaluated.

The result was that not even 1 square of the 100 1 mm x 1 mm squares in the checker-board pattern was peeled off.

Actual Example 2

The additives were added, drying and pelletizing were performed, the result was injection-molded, and sputtering was performed in the same manner as in Actual Example 1, except that 2.5 kg of the maleic-anhydride-modified hydrogenated styrene-butadiene block copolymer obtained by the graft reaction of Actual Example 1 and 2.5 kg of the polymer obtained in Resin Manufacturing Example 1 were used.

The softening point of the substrate resin was 163°C, and its bending modulus was 23,000 kg/cm².

The result of the tape peeling test performed in the same manner as in Actual Example 1 was that none of the 100 squares was peeled off.

Actual Example 3

The same reaction as the graft reaction of Actual Example 1 was performed, except that 3 kg of the hydrogenated polystyrene obtained in Resin Manufacturing Example 1 were used; a maleic-anhydride-modified hydrogenated polystyrene was obtained. The maleic anhydride content in this modified polymer was 0.9 wt %. Moreover, almost no change was observed in the molecular weight before and after the graft reaction.

Three kg of the maleic-anhydride-modified hydrogenated polystyrene obtained in this manner and 2 kg of the hydrogenated styrene-butadiene block copolymer obtained in Resin Manufacturing Example 2 were dissolved in tetrahydrofuran and then co-precipitated in methanol. The remaining operations were performed in the same manner as in Actual Example 1 (adding the additives, pelletizing, injection molding, and sputtering).

The softening point of the substrate resin was 163°C, and its bending modulus was 25,000 kg/cm².

The result of the tape peeling test was that not 1 square of the 100 squares was peeled off.

Actual Example 4

The same reaction as the graft reaction of Actual Example 1 was performed, except that the polymer obtained in Resin Manufacturing Example 3 (number average molecular weight 89,000, butadiene content 8 wt %) was used; a maleic-anhydride-modified hydrogenated styrene-butadiene block copolymer was obtained. The maleic anhydride content in this modified polymer was 1.3 wt %, the number average molecular weight was 82,000.

This maleic-anhydride-modified hydrogenated styrene-butadiene block copolymer was dissolved in tetrahydrofuran and then precipitated in methanol. The remaining operations were performed in the same manner as in Actual Example 1 (adding the additives, pelletizing, injection molding, and sputtering).

The softening point of the substrate resin was 170°C, and its bending modulus was 26,000 kg/cm².

The result of the tape peeling test was that not 1 square of the 100 squares was peeled off.

Comparison Example 1

The same additives as in Actual Example 1 were added to hydrogenated polymer obtained in Resin Manufacturing Example 1, and the pelletizing, injection molding, and sputtering were performed in the same manner. The softening point of the substrate resin was 172°C, and its modulus of elasticity was 32,000 kg/cm².

The result of the tape peeling test was that 100 of the 100 squares were peeled off.

Comparison Example 2

The same reaction as the maleic anhydride graft reaction of Actual Example 1 was performed, using the polymer obtained in Resin Manufacturing Example 1; a maleic-anhydride-modified hydrogenated polystyrene was obtained. The maleic anhydride content of this modified polymer was 1.6 wt %.

The additives were added to this polymer and pelletizing, injection molding, and sputtering were performed in the same manner as in Actual Example 1. The softening point of the substrate resin was 172°C, and its bending modulus was 32,000 kg/cm².

The result of the tape peeling test was that 100 of the 100 squares were peeled off.

Table 1

	Softening point (°C)	Bending modulus (kg/cm ²)	Number of peeled squares (out of 100 squares)
Actual Example 1	168	25,000	0
2	163	23,000	0
3	163	25,000	0
4	170	26,000	0
Com- parison Example 1	172	32,000	100
2	172	32,000	100

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